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(71)Applicant : DAINIPPON TORYO CO LTD

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(72)Inventor : KUNIMATSU MASAOKI

SUGAWA TETSUO

SHIROTA TSUNEO

NAKATSU KATSUTAKA

(54) WATER-BASE FLUORESCENT INK FOR JET PRINTING AND METHOD FOR MARKING THEREWITH

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a fluorescent ink which leaves a large amount of a fluorescent dye on the surface of a substrate to increase the concentration of the dye on the surface and to thereby form images having high fluorescent intensity on the surface.

SOLUTION: This ink contains water-dispersible acrylic resin microparticles having a mean particle diameter of 0.05-0.5,  $\mu$ m, a water-soluble resin and a fluorescent dye which absorbs substantially no excitation energy at a wavelength of 400-600nm and absorbs excitation energy at a wavelength of 650-900nm to emit fluorescence. This method comprises printing the surface of a substrate with this ink by means of a ink jet printer and irradiating the surface with excitation energy at a wavelength of 650-900nm to allow the prints to emit fluorescence.

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**[Claim(s)]**

[Claim 1] jet printing characterized by containing fluorescent dye which hardly absorbs excitation energy with a water-dispersion-acryl-resin particle with a mean particle diameter of 0.05-0.5 micrometers, a water soluble resin, and a wavelength of 400-600nm, but absorbs excitation energy with a wavelength of 650-900nm, and emits fluorescence -- service water -- sex fluorescence ink.

[Claim 2] Aquosity fluorescence ink for jet printing according to claim 1 which makes it the feature to contain a water-dispersion-acryl-resin particle and to contain 5 - 35 % of the weight, and fluorescent dye for water soluble resin 0.001 to 5% of the weight 60 to 90% of the weight on ink solid content criteria.

[Claim 3] A firefly luminescence marking method characterized by printing on the printing hand-ed surface with an ink jet printer using aquosity fluorescence ink containing fluorescent dye which hardly absorbs excitation energy with a water-dispersion-acryl-resin particle with a mean particle diameter of 0.05-0.5 micrometers, a water soluble resin, and a wavelength of 400-600nm, but absorbs excitation energy with a wavelength of 650-900nm, and emits fluorescence, irradiating excitation energy with a wavelength of 650-900nm, and carrying out firefly luminescence on the printing surface.

**[Detailed Description of the Invention]**

**[0001]**

[The technical field to which invention belongs] jet printing which carries out firefly luminescence by this invention's being able to make high fluorescent dye concentration of the printing hand-ed surface, and irradiating excitation energy -- service water -- it is related with the firefly luminescence marking method which carries out firefly luminescence by irradiating sex fluorescence ink and excitation energy.

**[0002]**

[Description of the Prior Art] The fluorescence ink for jet printing used for the method of printing on the printing hand-ed surface with an ink jet printer using the ink containing fluorescent dye, and forming the mark of printing which carries out firefly

luminescence by the exposure of excitation energy, such as ultraviolet radiation and infrared light, a graphic form, a bar code, etc. on the printing surface, and such a method is indicated by official reports, such as JP,62-5079,B, JP,62-24024,B, and \*\*\*\*\* No. 500590 [ six to ], and is well-known.

[0003]

[Problem(s) to be Solved by the Invention] however, about a method or fluorescence ink given in these official reports In using the base material surface which has the absorbency of paper, cloth, etc. as a printing hand-ed Since the fluorescent dye in ink permeated and diffused to the printing hand-ed deep part with the solvent, when the concentration of the fluorescent dye in the printing hand-ed surface fell, and firefly luminescence reinforcement became inadequate, especially the printing hand-ed [ absorbent ] was colored by Japanese ink etc., there was a trouble that this orientation was remarkable. Moreover, it was economically [ operationally or ] difficult to make high concentration of the fluorescent dye in the printing hand-ed surface.

[0004] jet printing used for the firefly-luminescence marking method and it which it is made a lot of fluorescent dye remain on the printing-hand-ed surface, namely, can form an image with high firefly-luminescence reinforcement by the exposure of excitation energy for the purpose of this invention solving the trouble in the firefly luminescence marking method or fluorescence ink by the ink jet printer of the conventional technology which was described above -- service water -- it aims at offering sex fluorescence ink.

[0005]

[Means for Solving the Problem] A result of having studied many things in order that this invention persons might solve the above-mentioned technical problem, When it prints on the printing hand-ed surface with an ink jet printer using aquosity fluorescence ink which made a water-dispersion-acryl-resin particle contain Since it fixes without this particle permeating a printing hand-ed deep part on the printing hand-ed surface and fluorescent dye tends to adhere to the surface of these particles even if the printing hand-ed surface is the base material surface with the absorbency of paper, cloth, etc. Osmosis of fluorescent dye to a printing hand-ed deep part decreased, and, as a result, fluorescent dye concentration of the printing hand-ed surface became high, therefore knowledge that a high mark of firefly luminescence reinforcement was formed of an exposure of excitation energy was acquired, and this invention was completed.

[0006] namely, jet printing of this invention -- service water -- sex fluorescence ink is characterized by containing fluorescent dye which hardly absorbs excitation energy with a water-dispersion-acryl-resin particle with a mean particle diameter of 0.05-0.5

micrometers, a water soluble resin, and a wavelength of 400-600nm, but absorbs excitation energy with a wavelength of 650-900nm, and emits fluorescence.

[0007] Moreover, a firefly luminescence marking method of this invention is printed on the printing hand-ed surface with an ink jet printer using aquosity fluorescence ink containing fluorescent dye which hardly absorbs excitation energy with a water-dispersion-acryl-resin particle with a mean particle diameter of 0.05-0.5 micrometers, a water soluble resin, and a wavelength of 400-600nm, but absorbs excitation energy with a wavelength of 650-900nm, and emits fluorescence, and is characterized by irradiating excitation energy with a wavelength of 650-900nm, and carrying out firefly luminescence on the printing surface.

[0008] This invention is explained concretely below. Aquosity fluorescence ink for jet printing of this invention can use as an indispensable component water as fluorescent dye which has a water-dispersion-acryl-resin particle which has the specific mean particle diameter, water soluble resin, and the specific absorption property, and a solvent, can contain it, and can contain a water miscibility organic solvent, various additives, etc. if needed further.

[0009] A water-dispersion-acryl-resin particle used by this invention is a component blended in order to make high fluorescent dye concentration of the printing hand-ed surface and to make a high mark of firefly luminescence reinforcement form. Namely, although fluorescent dye permeates in the case of a printing hand-ed with absorbency and it is easy to diffuse it with a solvent at a deep part of a printing hand-ed in it, if a water-dispersion-acryl-resin particle is blended into fluorescence ink A front stirrup of jet printing of a particle which these particles remain without permeating a deep part of a printing hand-ed on the surface, and remains on the printing hand-ed surface adsorbs fluorescent dye at the time of jet printing. A mark which it controls that fluorescent dye permeates a printing hand-ed deep part, consequently fluorescent dye concentration of the printing hand-ed surface becomes high, therefore shows high firefly luminescence reinforcement by the exposure of excitation energy is formed.

[0010] Since it is hard coming to remain on the surface of a printing hand-ed and the interior of a printing hand-ed is permeated, it becomes impossible for the above-mentioned effect to demonstrate such a water-dispersion-acryl-resin particle enough, if mean particle diameter of a water-dispersion-acryl-resin particle is set to less than 0.05 micrometers. Therefore, in order for a water-dispersion-acryl-resin particle to remain on the surface of a printing hand-ed, the mean particle diameter needs to be 0.05 micrometers or more. On the other hand, in order for nozzle plugging of an ink jet printer not to arise, mean particle diameter of a water-dispersion-acryl-resin particle needs to be 0.5 micrometers or less.

[0011] In this invention, although emulsion resin which is made to carry out the emulsion polymerization of the alpha and beta-ethylene nature partial saturation monomer known widely by the bottom of existence of an emulsifier and a radical initiator and underwater, and is obtained from the former as a water-dispersion-acryl-resin particle can be used, when an emulsifier enters into ink, it becomes easy to generate a bubble in ink, and trouble may be caused to homogeneous marking formation. Therefore, in this invention, especially a thing for which generating of a bubble in the inside of ink is prevented is desirable by using a water-dispersion-acryl-resin particle which was made to use and carry out the emulsion polymerization of the reactant emulsifier, and obtained it instead of the usual emulsifier.

[0012] In addition, itself has alpha and beta-ethylene nature partial saturation monomer etc. and a functional group to which it can react it not only presents an emulsification operation chiefly, but, and a reactant emulsifier means what is incorporated in a frame of a polymer through a reaction by this functional group. Specifically, a compound which has polymerization nature partial saturation double bonds, such as acrylic ester (meta) of alpha, beta-unsaturated-carboxylic-acid monoester, an alkylene oxide addition product of an acrylic acid (meta), and polyoxyalkylene monoallyl ether, a vinyl sulfonic acid, sulfoalkyl (meta) acrylate, allyl compound alkyl itaconate sulfates, or these salts, is mentioned. It is appropriate for a reactant emulsifier to carry out 0.3-10 weight section use to the alpha and beta-ethylene nature partial saturation monomer 100 weight section.

[0013] As an aforementioned alpha and beta-ethylene nature partial saturation monomer A methyl acrylate, an ethyl acrylate (meta), butyl acrylate (meta), (Meta) Acrylic ester, such as 2-ethylhexyl acrylate and acrylic-acid (meta) lauryl (meta); Vinyl acetate, (Meta) Vinyl ester, such as propionic-acid vinyl; Aromatic series vinyl monomer; ethylene, such as styrene and vinyltoluene, Olefins, such as a propylene; Diallyl phthalate, a divinylbenzene, A monomer which has partial saturation double bonds, such as allyl compound acrylate; Glycidyl (meta) acrylate, (Meta) Functional-group content monomers, such as an acrylic acid, acrylic-acid (meta) hydroxyethyl, N-methylol (meta) acrylamide, and acrylic-acid (meta) dimethylaminoethyl, or two or more sorts of such mixture are mentioned. make it any -- if it distributes to stability in ink, various acrylic resin particles are usable.

[0014] Water soluble resin used by this invention is a component blended in order that a particle which adhered to a nozzle of an ink jet printer further in order to make stability distribute fluorescent dye and a water-dispersion-acryl-resin particle in ink, to improve the storage stability of ink and to be able to perform homogeneous marking formation, and in order to make it a water-dispersion-acryl-resin particle adhere to the printing

hand-ed surface firmly may enable it to remove simply.

[0015] A limit does not have especially a thing currently generally used in ink or coatings as water soluble resin, either, it can use it, and, specifically, polyacrylic acid, polyacrylate, a styrene-maleic-acid copolymer, a styrene sulfonic-acid-maleic-acid copolymer, polyester, hydroxyethyl cellulose, polyvinyl alcohol, a malto sill cyclodextrin, a polyethylene glycol, etc. are mentioned as a typical thing.

[0016] Fluorescent dye used by this invention is fluorescent dye which hardly absorbs excitation energy with a wavelength of 400-600nm, but absorbs excitation energy with a wavelength of 650-900nm, and emits fluorescence. That is, although it is hard to check by looking in a light exposure, it is fluorescent dye to which firefly luminescence is carried out in an infrared light exposure, and a check by looking becomes easy. Specifically, DTTCI (CAS registration number 3071-70-3) and HDITCI (CAS registration number 23178-67-8) which are a laser color, IR-125 (CAS registration number 3599-32-4), IR-132 (CAS registration number 62669-62-9), IR-140 (CAS registration number 53655-17-7), H.I.D.C. Iodide, etc. are mentioned as a typical (CAS registration number 36536-22-8) thing. In addition, since background fluorescence of a printing hand-ed interferes in a color which carries out firefly luminescence with excitation energy with short wavelength like ultraviolet radiation, it is unsuitable in this invention.

[0017] A solvent used in this invention is water, it is distilled water or ion exchange water preferably, and it is also possible to use together a part of water miscibility organic solvents, such as methyl alcohol, ethyl alcohol, isopropyl alcohol, dioxane, an acetone, a methyl ethyl ketone, carbitol, and dimethyl sulfoxide, if needed further. Fluorescence ink of this invention contains a component explained above as an indispensable component. About these blending ratio of coal A water-dispersion-acryl-resin particle on ink solid content criteria 60 - 90 % of the weight, It is preferably suitable for ink solid content that 10 - 30 % of the weight and fluorescent dye are 0.05 - 1 % of the weight preferably, and water soluble resin is [ fluorescent dye ] 25 - 46 % of the weight preferably ten to 50% of the weight 0.001 to 5% of the weight five to 35% of the weight 70 to 86% of the weight.

[0018] in addition, jet printing of this invention -- service water -- sex fluorescence ink can contain additives, such as dispersants, such as electric conductivity regulators, such as a lithium nitrate, a nitrous-acid lithium, ammonium sulfite, ammonium formate, ammonium acetate, lithium halide, and thiocyanic acid soda, and an amine denaturation silicone system dispersant, and antiseptics, in 0.1 - 5% of the weight of an amount further.

[0019] moreover, jet printing of this invention -- service water -- sex fluorescence ink

needs to have a property which was adapted for printing by ink jet printer. therefore, jet printing of this invention -- service water -- as for sex fluorescence ink, it is desirable for viscosity to be the range whose about 0.8 to 1.2 surface tension about 50 to 3000 ohm-cm and specific gravity is about 20-60 dynes/cm for about one to 10 mPa-sec (20 degrees C) and specific resistance.

[0020] Aquosity fluorescence ink for jet printing of this invention carries out mixed stirring of all the above-mentioned components at once, or carries out mixed stirring of fluorescent dye, a water-dispersion-acryl-resin particle, water soluble resin, and some solvents beforehand, makes fluorescent dye stick to a particle, carries out mixed stirring of these and the remainder component, and can prepare them by filtering and refining with a filter which has about 1 / ten or less pore-size of a diameter of a nozzle of an ink jet printer subsequently used. In this invention, a method which various well-known printers can be used [ method ] from the former as an ink jet printer, for example, makes ink breathe out by electric charge control system, ink on demand, and thermal head is held as a typical thing.

[0021] In a firefly luminescence marking method of this invention, a mark is formed by printing in a gestalt which is made to breathe out the aforementioned aquosity fluorescence ink with an ink jet printer on the printing hand-ed surface, and asks for it on it. Thus, by having turned marking up and irradiating excitation energy with a wavelength of 650-900nm, firefly luminescence of the mark is carried out and it becomes possible to decipher a mark by devices, such as viewing or an optical detector.

[0022]

[Example] An example and the example of a comparison explain this invention below at details.

After mixing fluorescent dye, a water-dispersion-acryl-resin particle, water soluble resin, and a solvent to homogeneity by the blending ratio of coal (unit: weight section) shown in one to examples 1-3 and example of comparison 5 table 1, the pore size 5.0micrometer membrane filter filtered and refined, and the fluorescence ink corresponding to each example and the example of a comparison was prepared. Dot printing was carried out at the postcard which smeared away the postcard each ink of whose is not printed with an ink jet printer, and its surface in India ink, the excitation light of the wavelength shown in a table 1 at the printing was irradiated, and firefly luminescence reinforcement was measured using the spectrophotofluorometer. The result is shown in the lower berth of a table 1.

[0023] In addition, in an example 1 and the examples 1-2 of a comparison, the firefly luminescence reinforcement in the non-printed postcard of the example 2 of a comparison was shown as a relative value at the time of being referred to as 100.

Moreover, in an example 2 and the examples 3-4 of a comparison, the firefly luminescence reinforcement in the non-printed postcard of the example 4 of a comparison was shown as a relative value at the time of being referred to as 100. Moreover, in the example 3 and the example 5 of a comparison, the firefly luminescence reinforcement in the non-printed postcard of the example 5 of a comparison was shown as a relative value at the time of being referred to as 100. Moreover, visual observation of the condition of the ink after standing was carried out for each ink for one month at the room temperature. The result is shown in the lower berth of a table 1. In addition, the error criterion is as follows.

O Abnormalities[ in :]-less x : after sedimentation of a resin particle or a color and separation having applied each ink to the glass plate in order that they might investigate the removal nature, when generating and a nozzle produced ink plugging, and making it dry, it was underwater immersed for 1 minute and the remelting nature of ink was investigated. The result is shown in the lower berth of a table 1. In addition, the error criterion is as follows.

O : remelt ink, and don't remain in a glass plate, but x:ink remains in a glass plate.

[0024]

[A table 1]

表 1

組 成		実施例 1	比較例 1	比較例 2	実施例 2	比較例 3	比較例 4	実施例 3	比較例 5
水分散性アクリル樹脂粒子 (数平均分子量50万~60万; 平均 粒子径 0.2~0.3 $\mu$ m; 酸価 0)		30	36		35	40		30	
水溶性樹脂	スチレン-マレイン酸共重合体	10		30					
	ポリビニルアルコール							5	10
	マルトシルサイクロデキストリン				10		30		
溶媒	イオン交換水	49	49	59	44	45	60	54	74
	エチルアルコール	5	7	5	5	10	5	10	15
	ジメチルスルホキシド	5	7	5	5	5	5		
蛍光染料	IR-140				0.1	0.1	0.1		
	IR-125	0.05	0.05	0.05					
	I. D. C. Iodide							0.02	0.02
性能試験	照射励起エネルギーの波長	795	795	795	825	825	825	655	655
	蛍光発光強度	無印刷ハガキ (A)	145	145	100	150	150	100	145
		墨塗りハガキ (B)	20	25	5	40	40	10	25
		蛍光発光強度比 (B)/(A) (%)	14	17	5	27	27	10	17
	貯蔵安定性	○	×	○	○	×	○	○	○
	再溶解性	○	×	○	○	×	○	○	○

[0025] The clear passage, the examples 1, 2, and 3 which are ink of this invention had all high firefly luminescence reinforcement, were high, and were still better than a table



1. [ of storage stability and remelting nature ] [ of the firefly luminescence intensity ratio to the non-printed postcard of a Japanese ink coating postcard ] The examples 1 and 3 of a comparison which do not blend water soluble resin on the other hand had storage stability and poor remelting nature. Moreover, the examples 2, 4, and 5 of a comparison which do not blend a water-dispersion-acryl-resin particle had low firefly luminescence reinforcement, and were low. [ of the firefly luminescence intensity ratio to the non-printed postcard of a Japanese ink coating postcard ]

[0026]

[Effect of the Invention] Even if it prints with an ink jet printer to an absorbency printing hand-ed, the fluorescent dye concentration in the printing hand-ed surface becomes high, and the aqueous fluorescence ink for jet printing of this invention can form the high mark of firefly luminescence reinforcement.